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(Name of document) SPECIFICATION

(title of the invention) a method of developing a resist film and a resist development processor

(Claims)

5 (Claims)

A resist development processor comprising:

a development processing chamber for storing a resist substrate having an exposed resist on the substrate and for developing the exposed resist by means of a development solvent consisting of a supercritical fluid; and

a supercritical fluid container for storing a supercritical fluid, said supercritical fluid container being connected to said development processing chamber through a valve.

(Claim 2)

A resist development processor comprising:

a high pressure gas container for storing a high pressure gas of said development solvent, said high pressure gas container being connected to said development processing chamber through a valve; and

a liquid container for storing said development solvent, said liquid container being connected through a valve.

25 (Claim 3)

The resist development processor according to Claim 2 characterized in that said high pressure gas container is provided with a back pressure regulator for ensuring that said development solvent in a gaseous state filled into said container is changed into a gas by opening of said valve, without allowing said supercritical fluid in said development processing chamber to be liquefied.

(Claim 4)

The resist development processor according to Claim 1 characterized in that said development processing chamber is provided with a temperature regulator for ensuring that a high pressure gas in said development processing chamber is removed, with the temperature of gas in said development processing chamber maintained above the temperature of critical point, thereby allowing the gas to be removed without being liquefied.

(Claim 5)

The resist development processor according to Claim 1 characterized by comprising resist substrate holding means that prevents said development solvent in liquid state from coming into contact with said resist substrate, when said liquid development solvent is introduced into said development processing chamber.

(Claim 6)

The resist development processor according to Claim
2 characterized in that said development processing
chamber is connected through a high pressure force
supply pump, in contact with said development solvent
5 in liquid state of said liquid container.
(Claim 7)

The resist development processor according to Claim
1 characterized in that said supercritical fluid
container is connected through a valve and a high
10 pressure force supply pump, in contact with said
liquid of the liquid container for storing said liquid
development solvent.
(Claim 8)

The resist development processor according to Claim
15 2 characterized in that said high pressure container
is connected through a valve, in contact with said gas
of the liquid container for storing said liquid and
gaseous development solvent.
(Claim 9)

20 The resist development processor according to Claim
1 further comprising a temperature regulator for
regulating the difference in the temperature of said
development solvent from each vessel, supplied to said
development processing chamber.
25 (Claim 10)

A resist development processing method characterized in that the development solvent consisting of supercritical fluid is introduced into a development processing chamber for storing a resist substrate having an exposed resist on the substrate, whereby development is carried out.

(Claim 11)

A resist development processing method characterized by comprising the steps of:

introducing the development solvent consisting of supercritical fluid into a development processing chamber for storing a resist substrate having an exposed resist on the substrate;

introducing the liquid of the same material as that of said fluid into said development processing chamber; and

removing said supercritical fluid from said development processing chamber.

(Claim 12)

A resist development processing method wherein development is performed by introduction of the development solvent consisting of supercritical fluid into a development processing chamber for storing a resist substrate having an exposed resist on the substrate, said resist development processing method

characterized by comprising the steps of:

filling the development processing chamber with the development solvent without contacting the resist substrate;

5 introducing said supercritical fluid into said development processing chamber;

pumping said development solvent in a liquid state into said development processing chamber; and

removing said supercritical fluid with the
10 temperature of gas in said development processing chamber maintained above the temperature of critical point, without allowing said supercritical fluid to be liquefied.

(Claim 13)

15 A resist development processing method comprising the steps of:

introducing liquid carbon dioxide into a development processing chamber for storing a resist substrate having an exposed resist and holding the
20 resist substrate to said gaseous carbon dioxide;

introducing supercritical carbon dioxide into said development processing chamber and maintaining it at a specified pressure, thereby allowing said development to be carried out;

25 pumping liquid carbon dioxide into said

development processing chamber and mixing it with said supercritical carbon dioxide;

discharging the supercritical carbon dioxide of said development processing chamber into a high

5 pressure carbon dioxide container filled with high pressure gaseous carbon dioxide, and converting the supercritical carbon dioxide filling said development processing chamber into gaseous form, thereby stopping said process of development; and

10 removing carbon dioxide of said development in the gaseous state.

(Claim 14)

The resist development processing method according to any one of Claims 10 through 13 characterized in
15 that changes in the temperature of said resist substrate in said development processing chamber do not exceed 10 degrees Celsius.

(Claim 15)

A surface processor comprising:

20 a processing chamber for storing an object to be processed;

a supercritical fluid container for storing a supercritical fluid, said supercritical fluid container being connected to said processing chamber
25 through a valve;

a high pressure gas container for storing the high pressure gas of the same material as that of said fluid, said high pressure gas container being connected to said processing chamber through a valve;

5 and

a liquid container for storing a liquid of the same material as that of said fluid, said liquid container being connected through a valve.

(Claim 16)

10 A surface processing method comprising the steps of:

introducing the supercritical fluid filled in the supercritical fluid container, into the processing chamber for storing an object to be processed;

15 introducing into the said processing chamber the liquid of the same material as that of said fluid filled in the liquid container; and discharging the supercritical fluid of said processing chamber into the high pressure gas container filled with high pressure gas.

20 (Detailed description of the invention)

(0001)

(Technical FIELD to which the invention pertains)

The present invention relates to a method of developing a resist film formed on a substrate such as
25 an LSI, a method of surface treatment of the resist

film, a development processor for the resist, and a surface processor.

(0002)

(Related art)

5 The following publications show related art of the present invention.

(1) Patent Document 1; Japanese Patent Laid-Open Publication No. 07-284739 (1995)

(2) Patent Document 2; Japanese Patent Laid-Open
10 Publication No. 09-139374 (1997)

(3) Patent Document 3; Japanese Patent Laid-Open Publication No. 11-87306 (1999)

(4) Patent Document 4; Japanese Patent Laid-Open Publication No. 01-220828

15 (0003)

In manufacturing a large-scale, high-integration density and high-performance device, a resist film, which is formed on a silicon wafer is exposed, developed, rinsed and dried to form a pattern thereon.

20 Then, a process comprising steps of etching the silicon, rinsing and drying is carried out to manufacture the above-mentioned device. In the specification, the resist is defined as the polymer material sensitive to light, X-ray, electron beam or
25 the like.

A special-purpose processing apparatus is required in each of these steps. Further, since chemical solutions such as a developer and a rinser have been used in development, rinsing and cleaning processes, a
5 drying step is essential after the rinsing and cleaning steps.

(0004)

Patent Document 1 discloses a rinsing apparatus for rinsing such micromachined parts as a
10 semiconductor and liquid crystal display where a rinsing medium of the supercritical state is used.

Patent Document 2 shows the method of rinsing with a supercritical fluid in the step of forming a microscopic structure or production of a semiconductor
15 device.

Patent Document 3 describes a drying apparatus using a supercritical fluid in the production of a semiconductor device.

Patent Document 4 indicates the method for forming
20 the pattern of a resist by development using a supercritical fluid.

(0005)

(Problems to be solved by the invention)

Patent Documents 1 through 3 disclose rinsing and
25 drying by a supercritical fluid, but fail to show

development of the substrate having an exposed resist, using a supercritical fluid.

The present inventors have found out the following problems in the above-mentioned drying process:

5 The pattern collapse may be caused by the action of surface tension of the above-mentioned chemical solution remaining in the pattern formed in the resist film.

When, in order to prevent the pattern from collapse, a
10 drying method using the supercritical carbon dioxide is used in the drying process for reducing the surface tension acting to the pattern, water remaining in the pattern cannot be completely removed even if the supercritical carbon dioxide is used as the drying
15 agent, subsequent to alkali development and water rinsing. The prior art method cannot prevent the pattern from collapse. For this reason, the present inventors have found it difficult to use the drying method using the above-mentioned supercritical fluid.

20 (0007)

The prevent inventors have also found out the following problems: In the development of the resist film having a microscopic structure with the supercritical fluid as shown in Patent Document 4,
25 carbon dioxide is introduced into the development

processing chamber by heating the development
processing chamber. As the heat capacity of the
chamber becomes larger, the time period for reaching
the temperature to the set level, which is above the
5 critical temperature at which the intended dissolution
power is exhibited is prolonged. That is, the intended
dissolution power becomes equal to the development
conditions. This leads to the failure to obtaining a
satisfactory result. Especially when a plurality of
10 large-diameter resist films each having a diameter of
200 mm or more are developed, some of the resist films
touch the liquid carbon dioxide when it is introduced.
This results in phenomena that are beyond the control,
thereby causing fluctuations in development.

15 (0008)

An object of the present invention is to provide a
method of developing a resist film, a method of
treating a surface of a resist film carried on a
substrate such as silicon wafer, a resist development
20 processor, and a surface processor that permit
microscopic development of the resist film in a short
period of time with the minimum fluctuation and
maximum accuracy, using such a supercritical fluid as
carbon dioxide that eliminates the need of utilizing a
25 chemical solution and waste liquid treatment facility.

(0009)

(Means for solving the problems)

The present inventors have found out an apparatus and the method for utilizing the same that ensure quick development of an exposed resist film with a supercritical fluid in the aforementioned process, using supercritical carbon dioxide, so as to eliminate the possibility of pattern collapse or the need of using a chemical developer or rinser. The aforementioned apparatus and method can carry out a pattern forming process by removing the photo-exposed resist film or the non photo-exposed portion in the phase of development.

(0010)

Dissolution power of the solvent for a solute depends on the temperature and density of the solvent. When a solvent is used as a developer of the resist film, the solvent as a developer may be beyond the critical point, i.e. the supercritical state under the condition for getting dissolution power suitable for developing the resist film. The density of the supercritical fluid can be changed by controlling its pressure and temperature; as a result, its dissolution power can be controlled freely.

(0011)

The supercritical fluid has the similar degree of diffusion power to that of gas, and can be changed from liquid to gas, without passing through the equilibrium line. To put it another way, fluid pressure is controlled below the critical level while the temperature of the fluid is kept above the critical temperature, whereby the fluid is changed from liquid to gaseous state. This change of the state does not bring about action of the surface tension.

10 (0012)

Such a substance as carbon dioxide that changes into gas at the normal temperature and atmospheric pressure and that has a relatively low critical pressure and temperature is suitable as a supercritical fluid for developing the resist film having a microscopic pattern. Carbon dioxide has a critical temperature of 31 degrees Celsius and a critical pressure of 7.3 MPa. A resist film made of fluorine-containing polymeric material that can be solved in liquid carbon dioxide or supercritical carbon dioxide is suitable as the solvent for the resist film.

20

(0013)

When carbon dioxide as development solvent is in the gaseous state, density is lower than the liquid

25

carbon dioxide and supercritical carbon dioxide.
Accordingly, dissolution power is extremely small.
Thus, the development effect on the resist film is
available only when carbon dioxide as development
5 solvent is in the supercritical or liquid state.
(0014)

To be more specific, when the development
processing chamber with a resist substrate placed
therein is filled with carbon dioxide in the liquid or
10 supercritical state, the resist is developed. If the
carbon dioxide filling the development processing
chamber is changed into gas, resist development is
discontinued because the resist is not dissolved. To
put it another way, the time when the development
15 processing chamber is filled with carbon dioxide in
the liquid or supercritical state is equal to the
resist development time.
(0015)

Resist development by supercritical carbon dioxide
20 is carried out as follows: A resist substrate, coated
with such a resist as a fluorine-containing polymeric
material that can be dissolved in carbon dioxide, is
exposed and installed in a development processing
chamber. Then development processing chamber is filled
25 with supercritical carbon dioxide, and the solubility

of supercritical carbon dioxide with respect to
fluorine-containing polymeric material is utilized for
resist development by supercritical carbon dioxide.
(0016)

5 Development is discontinued by discharging the
supercritical carbon dioxide from the development
processing chamber and reducing the pressure inside
the development processing chamber, thereby converting
carbon dioxide in a gaseous state. Further, when the
10 atmospheric pressure has been reached by discharging
carbon dioxide from the development processing chamber,
the resist substrate is taken out of the development
processing chamber to terminate the process of
development.

15 (0017)

 The solubility of carbon dioxide with respect to
fluorine-containing polymeric material is about the
same as that of hexane. Especially when developing a
plurality of large-diameter resist substrates having a
20 diameter of 200 mm or more, a large quantity of
supercritical carbon dioxide is required. The high
pressure container serving as a development processing
chamber is required to have a sufficient volume to
accommodate the amount of supercritical carbon dioxide
25 needed for development. This leads to an increase in

the size of the development processing chamber and heat capacity.

(0018)

5 The carbon dioxide serving as a development solvent is introduced into the development processing chamber from a siphon-based liquid carbon dioxide container in the liquid form. Then the development processing chamber is controlled to have the set temperature above the critical temperature, to ensure
10 that carbon dioxide is converted from liquid to supercritical state. Rise of temperature is accompanied by rise of pressure. The pressure in the development processing chamber is held to the set level of not less than the critical pressure, by the
15 back pressure regulator.

(0019)

 When carbon dioxide is introduced from the siphon-based liquid carbon dioxide container into the development processing chamber, liquid carbon dioxide
20 is led into the development processing chamber until both pressures are equal to each other. In this case, if the percentage of the liquid carbon dioxide filling the development processing chamber is below 50%, the supercritical state cannot be reached even if the
25 temperature in the development processing chamber is

raised over the critical temperature.

(0020)

The percentage of liquid carbon dioxide in the development processing chamber depends on the saturated vapor pressure characteristics of carbon dioxide. Accordingly, when the temperature of the siphon-based liquid carbon dioxide container is controlled so as to exceed 25 degrees Celsius, then the internal pressure will be at least 6 MPa. If the temperature in the development processing chamber is controlled to reach the level of about 20 degrees Celsius, then the percentage of the liquid carbon dioxide filling the development processing chamber will reach about 80%. If the temperature in the development processing chamber is raised to about 35 degrees Celsius under this condition, the chamber will be filled with supercritical carbon dioxide of about 10 MPa.

(0021)

For the aforementioned reasons, the temperature in the development processing chamber must be controlled to reach the level of 20 degrees Celsius when liquid carbon dioxide is introduced into the development processing chamber. Thus, a large quantity of heat must be supplied when the temperature of the

development processing chamber having a sufficient volume to develop a plurality of large-diameter resist substrates having a diameter of 200 mm or more is raised above the critical temperature. This will
5 require a long time, as shown in Fig. 2. The control time from introduction of liquid carbon dioxide to the arrival to the set temperature level can be simply calculated from the heat capacity of the high pressure container, the capacity of the heater and heat
10 transfer efficiency. It is apparent that a smaller heat capacity of the development processing chamber leads to less time to change the carbon dioxide filling the development processing chamber from liquid to supercritical state. However, this involves an
15 increase in the heat capacity of the development processing chamber. This problem and the problems involved in the development of a plurality of large-diameter resist substrates having a diameter of 200 mm or more are solved by the following apparatus and the
20 method for the same:

(0022)

The present invention provides a resist development apparatus comprising:

a development processing chamber for storing a
25 resist substrate having an exposed resist on the

substrate and for developing the exposed resist by means of a development solvent consisting of a supercritical fluid; and

5 a supercritical fluid container for storing a supercritical fluid, this supercritical fluid container being connected to this development processing chamber through a valve. The present invention is further characterized by containing:

10 a high pressure gas container for storing a high pressure gas, this high pressure gas container being connected to this development processing chamber through a valve; and

15 a liquid container for storing the liquid liquefied by high pressure, this liquid container being connected through a valve.

(0023)

To be more specific, the present invention provides a resist development processor that utilizes the solubility of a supercritical fluid introduced
20 into the development processing chamber where an exposed resist substrate is installed. It is characterized in that supercritical fluid is filled into a supercritical fluid container connected by a pipe to the development processing chamber through a
25 valve; and the development processing chamber is

filled with the supercritical fluid of a predetermined density and temperature when the valve is opened. It is preferred that the present invention be equipped with:

- 5 a back pressure regulator wherein the high pressure container connected by a pipe to this development processing chamber through a valve is filled with high-pressure development solvent, and supercritical fluid having filled the development
10 processing chamber is converted into gaseous state without being liquefied, when the valve is opened;
 a temperature regulator for ensuring that, when the high pressure gas filling the aforementioned resist development processing chamber is discharged,
15 it can be discharged while the gas temperature in the resist development processing chamber is controlled so as to exceed the critical point, whereby gas is discharged from the resist development processing chamber without being liquefied;
- 20 holding means that, when liquid serving as a development solvent is introduced into the aforementioned development or when the pressure of the resist development processing chamber is boosted, prevents the liquid development solvent from coming
25 into contact with the resist substrate;

a high pressure force supply pump that pumps liquid development solvent into the aforementioned resist drying chamber; and

5 a temperature regulator for regulating so as to minimize the difference in the temperatures of the aforementioned development solvents supplied into the aforementioned development processing chamber from each container.

(0024)

10 The present invention also provides a resist development processing method for performing development by direct introduction of development solvent consisting of supercritical fluid into a resist substrate having an exposed resist on the
15 substrate.

(0025)

The present invention also provides a resist development processing method characterized by comprising the steps of:

20 introducing the supercritical fluid into the development processing chamber for storing a resist substrate having an exposed resist on the substrate;

introducing the liquid of the same material as that of the aforementioned fluid into the
25 aforementioned development processing chamber; and

removing the aforementioned supercritical fluid
from the development processing chamber.

(0026)

To put it more specifically, the present invention
5 provides a resist development processing method
wherein development is performed by introduction of
the development solvent consisting of supercritical
fluid into a development processing chamber for
storing a resist substrate having an exposed resist on
10 the substrate. This resist development processing
method is characterized by comprising the steps of:

filling the development processing chamber with
the development solvent without contacting the resist
substrate;

15 introducing the supercritical fluid into the
development processing chamber;

pumping the development solvent in a liquid state
into the development processing chamber; and

removing the supercritical fluid with the
20 temperature of gas in the development processing
chamber maintained above the temperature of critical
point, without allowing the supercritical fluid to be
liquefied.

The present invention further provides a resist
25 development processing method comprising the steps of:

introducing liquid carbon dioxide into a development processing chamber for storing a resist substrate having an exposed resist and holding the resist substrate to the aforementioned gaseous carbon dioxide;
5

introducing supercritical carbon dioxide into the aforementioned development processing chamber and maintaining it at a specified pressure, thereby allowing the aforementioned development to be carried out;
10

pumping liquid carbon dioxide into the aforementioned development processing chamber and mixing it with the aforementioned supercritical carbon dioxide;

15 discharging the supercritical carbon dioxide of the aforementioned development processing chamber into a high pressure carbon dioxide container filled with high pressure gaseous carbon dioxide, and converting the supercritical carbon dioxide filling the
20 aforementioned development processing chamber into gaseous form, thereby stopping the process of development; and

removing carbon dioxide of the aforementioned development in the gaseous state.

25 In the method according to the present invention,

the temperature of the development solvent into the development processing chamber is adjusted in such a way that changes in the temperature of the resist substrate in the aforementioned development processing chamber do not exceed 10 degrees Celsius, preferably, 5 degrees Celsius.

(0027)

The present invention further provides a surface processor comprising:

10 a processing chamber for storing an object to be processed;

a supercritical fluid container for storing a supercritical fluid where this supercritical fluid container is connected to the processing chamber through a valve;

15 a high pressure gas container for storing the high pressure gas of the same material as that of the aforementioned fluid where the high pressure gas container is connected to the aforementioned processing chamber through a valve; and

20 a liquid container for storing a liquid of the same material as that of the aforementioned fluid where the liquid container is connected through a valve.

25 (0028)

In the method according to the present invention, the temperature of the development solvent into the development processing chamber is adjusted in such a way that changes in the temperature of the resist substrate in the aforementioned processing chamber do not exceed 10 degrees Celsius, preferably 5 degrees Celsius.

(0029)

The present invention further provides a surface processor comprising:

a processing chamber for storing an object to be processed;

a supercritical fluid container for storing a supercritical fluid where this supercritical fluid container is connected to the processing chamber through a valve;

a high pressure gas container for storing the high pressure gas of the same material as that of the aforementioned fluid where the high pressure gas container is connected to the aforementioned processing chamber through a valve; and

a liquid container for storing a liquid of the same material as that of the aforementioned fluid where the liquid container is connected through a valve.

(0030)

The present invention further provides a surface processing method comprising the steps of:

introducing the supercritical fluid filled in the supercritical fluid container, into the processing chamber for storing an object to be processed;

introducing into the aforementioned processing chamber the liquid of the same material as that of the aforementioned fluid filled in the liquid container; and

discharging the supercritical fluid of the processing chamber into the high pressure gas container filled with high pressure gas.

(0031)

The resist development apparatus and the method thereof, using supercritical fluid according to the present invention, ensures precise control of the solubility of a supercritical fluid as a development solvent. In the formation of a minute pattern having a resist width of 100 nm through 20 nm (for future), this invention permits development of the resist pattern without variation where high-performance characteristics are required. Alternatively, the surface processor and the method thereof allow quick processing in the phase of cleaning and drying, separately from the aforementioned development, and

are capable of meeting the requirements in minute pattern formation.

(0032)

(THE PREFERRED EMBODIMENTS for practicing the
5 invention)

Fig. 1 is a block diagram representing a supercritical resist development apparatus according to the present invention. A supercritical carbon dioxide container 3 filled with supercritical carbon
10 dioxide 13 at a pressure of 20 MPa and a temperature of 40 degrees Celsius is connected through a valve 4 to the development processing chamber 1 controlled to have a temperature of 30 degrees Celsius. After a resist substrate 5 coated with exposed fluorine-
15 containing polymeric material has been installed in the substrate holder 6 inside the development processing chamber 1, the development processing chamber 1 is enclosed with a cover 2. The valves 4, 8, 11, 12 and 23 connected to the development processing
20 chamber 1 are closed and a valve 20 connected to the high pressure carbon dioxide gas container 10 is opened.

(0033)

When the siphon-based liquid carbon dioxide
25 container 9 is controlled to 25 degrees Celsius by the

temperature regulator 22, the internal pressure can be set to 6 MPa because of the saturated vapor pressure characteristics of carbon dioxide. If the valve 8 is opened, liquid carbon dioxide 14 is introduced into the development processing chamber 1 from the siphon-based liquid carbon dioxide container 9. If the pressure of the development processing chamber 1 has reached the same pressure of the siphon-based liquid carbon dioxide container 9, the valve 8 is closed. Since the development processing chamber 1 is controlled to 36 degrees Celsius, the liquid carbon dioxide introduced is turned into gas because of the saturated vapor pressure characteristics, and the development processing chamber is filled with gas carbon dioxide having a pressure of 6 MPa and a temperature of 36 degrees Celsius.

(0034)

The supercritical carbon dioxide container 3 filled with supercritical carbon dioxide 13 having a temperature of 40 degrees Celsius and a pressure of 20 MPa is connected to the development processing chamber 1 through a valve 4. When the valve 4 is opened, the supercritical carbon dioxide 13 is introduced into the development processing chamber 1 and the development processing chamber 1 is filled with supercritical

carbon dioxide having a pressure of 14 MPa and a temperature of 38 degrees Celsius, thereby allowing the development of the resist substrate 5 to be started.

5 (0035)

When the pressure of the development processing chamber 1 has become equal to that of the supercritical carbon dioxide container 3, the valve 4 is closed. In this case, even if supercritical carbon dioxide filling the development processing chamber 1 has dissolved the resist, solubility is kept constant without changing. Accordingly, the valve 8 has opened, and the liquid carbon dioxide 14 is pumped into the development processing chamber 1 by the high pressure force supply pump 7 at the rate of 50 ml per minute. The liquid carbon dioxide introduced into the development processing chamber 1 is turned into supercritical state by heat transfer and is mixed with supercritical carbon dioxide filling the development processing chamber 1.

20 (0036)

The valve 12 opens concurrently as the pumping of liquid carbon dioxide has started the high pressure force supply pump 7. When liquid carbon dioxide is pumped by the high pressure force supply pump 7, the

25

pressure of the development processing chamber 1 is boosted. However, it is discharged by the back pressure regulator 33 set at 14 MPa, and the development processing chamber 1 is held to a set pressure of 14 MPa. After liquid carbon dioxide has been pumped by the high pressure force supply pump 7 for 200 seconds, the valve 8 is closed to discontinue pumping.

(0037)

10 To discontinue development, the state of carbon dioxide filling the development processing chamber 1 is changed into gas. The high pressure carbon dioxide gas container 10 filling the carbon dioxide gas 15 having a temperature of 36 degrees Celsius and a pressure of 4 MPa is connected to the development processing chamber 1 through the valve 11. When the valve 11 is opened for a short time, supercritical carbon dioxide filling the development processing chamber 1 is discharged into the high pressure carbon dioxide gas container 10. Supercritical carbon dioxide filling the development processing chamber 1 is changed into gas having a pressure of 6 MPa and a temperature of 35 degrees Celsius, whereby development is stopped. In this case, the pressure of the high pressure carbon dioxide gas container 10 is boosted by

the supercritical carbon dioxide introduced, but the gas is discharged from the back pressure regulator 26 and the pressure is maintained to 4 MPa.

(0038)

5 When development has been discontinued, the carbon dioxide filling the development processing chamber 1 is discharged. The valve 23 is opened to discharge carbon dioxide from the pressure control valve 24. When it is discharged, the development processing
10 chamber is controlled to a temperature of 36 degrees Celsius above the critical temperature in such a way that carbon dioxide filling the development processing chamber 1 is not be liquefied.

(0039)

15 When the pressure in the development processing chamber 1 has reached the atmospheric pressure, the development processing chamber cover 2 is opened to take out the resist substrate 5.

(0040)

20 Fig. 4 is a cross section representing part of the configuration of a resist development apparatus for filling the supercritical carbon dioxide container with supercritical carbon dioxide, according to the present invention. The supercritical carbon dioxide
25 container 3 is controlled to 20 degrees Celsius by a

temperature regulator 27. A siphon-based liquid carbon dioxide container 30 is installed separately from the siphon-based liquid carbon dioxide container 9 given in Fig. 1. The temperature is controlled to about 25
5 degrees Celsius by a temperature regulator 32. When valves 4 and 18 are closed and valve 19 is opened, the liquid carbon dioxide 31 is introduced into the supercritical carbon dioxide container 3. When the pressure of liquid carbon dioxide container 30 has
10 become equal to that of the supercritical carbon dioxide container 3, the valve 18 is opened and the liquid carbon dioxide 31 is pumped into the supercritical carbon dioxide container 3 by a high pressure force supply pump 29. Concurrently as pumping
15 of the high pressure force supply pump 29 has started, the supercritical carbon dioxide container 3 is controlled to 40 degrees Celsius by the temperature regulator 27, whereby the liquid carbon dioxide introduced in the supercritical carbon dioxide
20 container 3 is changed into supercritical carbon dioxide 13. The pressure is kept at 20 MPa by the back pressure regulator 25. When the carbon dioxide filling the supercritical carbon dioxide container 3 has reached a pressure of 20 MPa and a temperature of 40
25 degrees Celsius, filling operation terminates. The

siphon-based liquid carbon dioxide container 30 is installed separately from the siphon-based liquid carbon dioxide container 9 given in Fig. 1, and can be connected through the high pressure force supply pump 7 of the siphon-based liquid carbon dioxide container 9.

(0041)

Fig. 5 is a cross sectional view representing a part of the configuration of a resist development apparatus for filling the supercritical carbon dioxide gas container with supercritical carbon dioxide gas, according to the present invention. When the valve 21 is opened, carbon dioxide gas 36 is introduced until the pressures of liquid carbon dioxide container 34 and high pressure carbon dioxide gas container 10 are equal to each other. For the liquid carbon dioxide container 34, carbon dioxide gas introduced in excess of the set pressure of 4 MPa is discharged from the back pressure regulator 26 by opening the valve 20 and the pressure is kept at 4 MPa. The liquid carbon dioxide container 34 is installed separately from the liquid carbon dioxide container 9 given in Fig. 1, and can be connected to the gaseous portion of the liquid carbon dioxide container 9.

(0042)

Fig. 6 is a schematic diagram representing the state of carbon dioxide filling the development processing chamber during resist development by the resist development apparatus according to the present invention for filling the liquid carbon dioxide container with liquid carbon dioxide. During development, liquid carbon dioxide 14 is pumped into the development processing chamber 1 from the liquid carbon dioxide inlet 39 by the high pressure force supply pump 7. Immediately after introduction, it remains in the bottom of the development processing chamber in the liquid form. If the resist substrate holder is configured in a flat plate shape as shown in Fig. 7, the resist substrate 5 is immersed in liquid carbon dioxide 38, and development out of control will occur. To prevent the resist substrate 5 from being immersed in liquid carbon dioxide 38, the resist substrate holder 6 is shaped in a cut form, as shown in Fig. 6.

(0043)

Fig. 3 is a diagram representing the temperature state of carbon dioxide in the development processing chamber in this case. Development is started by opening the valve 4, and is stopped by opening the valve 11. As described above, supercritical carbon

dioxide is introduced into the development processing chamber and development is carried out.

When development is discontinued, the supercritical carbon dioxide is discharged in the gaseous form, whereby gaseous state is created in the development processing chamber, and development is stopped. To be more specific, much time is required to convert liquid carbon dioxide in supercritical carbon dioxide by heating the development processing chamber, as shown in Fig. 2. This gives rise to the time of development out of control. According to the present embodiment, however, such time hardly occurs. To put it another way, such time is minimized, and accurate setting of the development time is ensured according to the present embodiment, whereby the optimum development result can be obtained.

(0044)

According to the present embodiment, minute resist development can be controlled under the optimum resist development conditions by using the supercritical fluid such as carbon dioxide. Especially, this allows time control of the solubility of supercritical fluid used for development, thereby providing development results free from variations.

(0045)

As described above, the resist substrate coated with resist soluble in carbon dioxide such as fluorine-containing polymeric material after having been exposed can be developed by supercritical carbon dioxide. At the same time, use of a waste processing facility is eliminated since no chemical solution is used in the step of development processing.

(0046)

Further, as shown in the present embodiment, no chemical solution is used in the development and rinsing steps. This eliminates the need of using a prior art drying process, and avoids minute pattern collapse--a problem in the drying process. Further, in the aforementioned step of development processing according to the prior art, a plurality of processing facilities are required in each step of cleaning and drying at least in the subsequent process. By contrast, the present embodiment allows simultaneous processing of development, cleaning and drying to be performed by one and the same development processor.

(0047)

(Advantages of the invention)

According to the present invention, a plurality of large-diameter resist substrates having a diameter of 200 mm and more can be developed simultaneously under

the optimum resist development conditions, using supercritical fluid such as carbon dioxide. Especially the present invention provides time control of the solubility of the supercritical fluid used for development, and allows precise setting of development conditions.

As described above, the resist substrate coated with resist soluble in carbon dioxide such as fluorine-containing polymeric material after having been exposed can be developed by supercritical carbon dioxide. At the same time, use of a waste processing facility is eliminated since no chemical solution is used in the step of development processing.

Further, according to the present invention, no chemical solution is used in the development and rinsing steps. This eliminates the need of using a prior art drying process, and avoids minute pattern collapse--a problem in the drying process. Further, in the aforementioned step of development processing according to the prior art, a plurality of processing facilities are required in each step. By contrast, the present invention uses only one apparatus to handle these jobs.

(Brief description of the drawings)

Fig. 1 is a block diagram representing a resist development apparatus according to the present invention;

5 Fig. 2 is a diagram representing changes in the state of carbon dioxide in a resist development processing chamber;

Fig. 3 is a diagram representing changes in the state of carbon dioxide in the resist development processing chamber in Fig. 1;

10 Fig. 4 is a block diagram of a resist development apparatus of the present invention, representing connection between a supercritical carbon dioxide container and a liquid carbon dioxide;

15 Fig. 5 is a block diagram of a resist development apparatus of the present invention, representing connection between a high pressure carbon dioxide container and a liquid carbon dioxide;

Fig. 6 is a block diagram of a resist development apparatus of the present invention, representing the state of carbon dioxide in a resist development processing chamber; and

20 Fig. 7 is a block diagram of a resist development processing chamber as a comparative example,
25 representing the state of carbon dioxide in the resist

development processing chamber.

(Explanation of reference numerals)

1; developing chamber, 2; developing chamber lid, 3;
supercritical carbon dioxide container, 4, 11, 12, 18,
5 19, 20, 21, 23; valve, 5; resist substrate, 6, 40;
resist substrate holder, 7; high pressure force pump,
8; valve, 9, 30, 34; siphon based liquid carbon
dioxide container, 10; high pressure carbon dioxide
gas container, 13, 37; supercritical carbon dioxide,
10 14, 31, 38; liquid carbon dioxide, 15, 36; high
pressure carbon dioxide gas, 16, 17, 22, 27, 32;
temperature regulator, 24; pressure control valve, 25,
26, 33; back pressure adjuster, 28, 35; check valve,
29; high pressure force pump, 39; liquid carbon
15 dioxide entrance.

(Name of document) Abstract

(Summary)

(Problem)

An object of the present invention is to provide a
20 resist developing apparatus and a method therefor,
which is capable of developing the resist within a
short period of time with a high precision and a small
fluctuation, using a supercritical fluid that needs no
chemical reagents nor processing equipment for waste
25 liquids.

(Means of Solving the Problems)

The present invention provides a resist development processor consisting of a development processing chamber for storing a resist substrate having an exposed resist on the substrate and for
5 developing the exposed resist by means of a development solvent consisting of a supercritical fluid; and a supercritical fluid container for storing a supercritical fluid, where the supercritical fluid container is connected to the development processing
10 chamber through a valve.
(Selected Figure) Fig. 1